

Arsenic Speciation, Seasonal Transformations, and Co-distribution with Iron in a Mine Waste-Influenced Palustrine Emergent Wetland

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Arsenic is commonly associated with mined ores and thus may be detrimental to naturally occurring wetlands that reside in mine waste-impacted regions. Understanding the relationship between Fe and As in both the aqueous and solid phase is critical for assessing the risk As imposes on these sensitive ecosystems. Therefore, in this investigation, Fe (perceived to be a dominant factor in the cycling of As) and As were monitored seasonally in a mine waste-influenced wetland. Iron and As concentrations in the pore waters at the site were highly variable but were at the highest levels during the spring and summer months. Using X-ray absorption near edge structure (XANES) spectroscopy, we confirmed that arsenite, arsenic sulfides, and arsenate species were present in the soil-solids, all of which varied seasonally within the site. Additionally, the reactivity of Fe and As solid phases, as measured by selective sequential extractions, changed seasonally. Iron and As are positively correlated in the sodium acetate/acetic acid (carbonates), HCl (amorphous materials), hydroxylamine-hydrochloride/acetic acid (crystalline oxide), and hydrofluoric acid (silicate) extractable fractions; these pools also comprised the largest portions of extractable Fe and As. Consequently, arsenate and arsenite species detected using XANES spectroscopy are likely to be associated with carbonates in the summer, with iron (hydr)oxides in the fall and winter, and with silicates in the spring with each of these components playing an important role in As sequestration and availability within the site.

Introduction

Knowledge of Fe and As cycling in natural wetlands is needed for wetland preservation and to understand the role these ecosystems play in sequestering trace elements. Wetlands commonly diminish suspended solids, nutrient loads, and aqueous concentrations of heavy metals and other pollutants

(1–3). Wetlands have been used as repositories for sewage sludges, industrial wastes, and mine wastes (3, 4). In anoxic systems, such as wetlands, redox-sensitive elements such as Fe influence As and other contaminant cycles (5). Additionally, seasonally induced changes in physicochemical soil conditions will undoubtedly influence Fe stability and may directly influence the availability of As (6–10). Therefore, understanding solid- and aqueous-phase transformations of Fe in addition to As in wetlands is essential for clearly defining the risk As poses on these ecosystems.

Arsenic is a toxic and redox-sensitive trace element that is ubiquitous in the Coeur d'Alene mining district (11). Arsenic toxicity, bioavailability, and mobility vary depending on its oxidation state. For example, arsenate ($H_xAsO_4^{x-3}$) is frequently found under oxic conditions, whereas arsenite ($H_xAsO_3^{x-3}$) and arsenic sulfides occur under anoxic conditions (12, 13). In general, arsenite is considered the most biologically toxic and soluble form of arsenic found in the environment (14). Thus, determining the oxidation state of As is important in assessing its fate, mobility, and impact on wetlands or other ecosystems.

Arsenic may bind to many solid phases present in soils and sediments, such as hydrous oxides of Al, Fe, Mn (15, 16), calcite (17, 18), sulfides (19), kaolinite (20, 21), and montmorillonite (22–24). Recent investigations of As sorption on amorphous and crystalline iron (hydr)oxides illustrate the potential for As attenuation via interaction with these mineral surfaces (16, 25–29). In addition to the aforementioned studies, an increasing number of field investigations (6, 8, 10) have examined the relationship between Fe and As in lacustrine and riverine environments. However, a complete understanding of the availability, partitioning, and speciation of As as well as its affiliation with Fe in wetlands remains unresolved. Accordingly, this investigation elucidates the seasonal changes and relationship between Fe and As within a contaminated wetland upon altering physicochemical soil conditions. Solid-phase As speciation was achieved using X-ray absorption near edge structure (XANES) spectroscopy, and reactive Fe and As phases were monitored using selective sequential extractions (SSE). In addition, Fe and As in the aqueous phase were monitored using membrane-separated diffusion cells (referred to as peepers).

Experimental Section

Site Description. The Coeur d'Alene Wetlands are situated due west of the Cataldo Mission, on the Cataldo Mission Flats in northern Idaho (see Figure 1 in the Supporting Information). The site has been impacted by mine wastes that were deposited in the Coeur d'Alene Basin. From 1882 to 1960, over 72 million tons of mine wastes were released into the Coeur d'Alene River system (30). The wetland we investigated in this study was a Paleolustrine Emergent Wetland (31). In the United States, the overwhelming majority of wetlands are Paleolustrine (31, 32); therefore, investigating Fe and As at this site may have considerable implications to contaminated wetlands found throughout the United States.

Sample Collection/Preparation. Cores were taken from three locations at the site (sites 5, 10, and 15) at each sampling time; the top 0–2 cm of each core was homogenized, and triplicate subsamples were used for solid-phase analysis. The sampling sites were situated along a transect through the deepest part of the wetland protruding into a dense cattail (*Typha latifolia*) stand. Samples were collected from sites 5, 10, and 15 on March 5, 1998 (late winter); May 13, 1998 (spring); July 8, 1998 (early summer); September 15, 1998 (late summer); November 27, 1998 (fall); and January 25,

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1999 (early winter) for SSE analysis. Temperature measurements at the sediment–water interface from the interior of the wetland (site 10) were monitored daily using a Hobo XT temperature logger.

Cores were removed from the site using a 4 cm diameter PVC piston coring device, immediately capped, and placed upright into a N₂-purged sample transporter (33). Upon returning to the laboratory, the cores were sectioned into 2-cm intervals in a N₂-purged atmosphere glovebox, and each section was homogenized. The top 0–2 cm of the sediment is in contact with the overlying water column and is considered the most reactive soil fraction; therefore, it was analyzed in greatest detail.

Aqueous Phase Sampling. Membrane-separated diffusion cells (peepers) have been used to monitor metal ions in solution (34). Peepers used in this experiment were created following the procedures of La Force et al. (33). Aqueous samples were then removed from the peepers, acidified with concentrated HCl to a pH < 2, and kept on ice until analysis 3 h later. Additionally, on separate peepers we determined the pH of the water column. Samples were collected on March 16, 1998 (late winter); May 13, 1998 (spring); July 18, 1998 (summer); and November 28, 1998 (fall). A field blank of double-deionized water with 2 drops of concentrated hydrochloric acid (HCl) was also run with the samples as a quality control; metal concentrations in the blank were negligible.

Statistical Analysis. Peeper and SSE data from all three sites were analyzed using a SAS–GLM procedure and a SAS–CORR procedure (35) in order to determine, at the 95% confidence level ($P = 0.05$), the correlation coefficients in seasonal trends among the three sites for a given data set.

XANES Spectroscopic Analysis. X-ray absorption near edge structure spectroscopy is ideal for examining low concentrations of amorphous and crystalline components in soils and is conducted in a non-invasive environment. Recently, XANES spectroscopy has been used to speciate As in coal ash, soil, and mine tailings and as sorbed complexes on mineral surfaces (21, 36–38). In this investigation, sediment samples were mounted as wet pastes for As XANES spectroscopic analysis. Solids were mounted in acrylic plates and sealed with Kapton polyimide film to prevent moisture loss while minimizing X-ray absorption. Samples were collected for XANES spectroscopic analysis from the interior of the wetland (site 5) to assess As response to different physicochemical conditions. Unfortunately, on the basis of time constraints and limited access to synchrotron facilities, we could only analyze samples collected on April 22, 1998; June, 24, 1998; and December 17, 1998.

XANES spectroscopy was performed on beamlines IV-1, IV-2, and IV-3 (beamline IV is an 8 pole wiggler) at the SSRL running under dedicated conditions. The ring operated at 3 GeV with a current ranging from ≈ 100 to ≈ 50 mA. Energy selection was accomplished using a Si(220) monochromator with an unfocused beam. Depending on the beamline, higher-order harmonics were either eliminated by a harmonic rejection mirror or by detuning approximately 60%. Absorption spectra were recorded by fluorescent X-ray production using a wide-angle ionization chamber (39) for model compounds or a 13-element Ge semiconductor detector (40) for unknown samples. Germanium filters along with Soller slits were used to minimize the effects of scattered primary radiation. Incident and transmitted intensities were measured with in-line ionization chambers. Spectra were recorded over the energy range of -200 to 1000 eV about the K-edge of As (11867 eV). Each scan was calibrated internally by placing sodium arsenate between the second and third in-line ionization chambers, with the inflection points for arsenate set at 11 874 eV. Between 3 and 8 individual spectra were averaged for each sample.

Standards were used to identify unknown samples and include arsenic sulfides (arsenopyrite, realgar, and orpiment), sodium arsenite, and sodium arsenate. Arsenopyrite, realgar, and orpiment were purchased from Wards Scientific (Rochester, NY). Sodium arsenite and arsenate were purchased from Fischer Scientific (Santa Clara, CA). The purity of all mineral standards was confirmed using X-ray diffraction. Sodium arsenite and arsenate are common standards and are representative of most sorbed arsenic phases (38). Standards were chosen based on their likelihood for occurrence in the system.

Arsenic species were first quantified using peak positions of the Gaussian–Lorentzian components and comparing them to those of the standard compounds. Following data reduction, positioning of the maximum first-derivative curve intensities were used to differentiate between the different As components. For example, arsenate, arsenite, and arsenic–sulfur complexes are well separated from each other within first-derivative XANES spectra—at least 2 eV separates each type of complex (see Figure 2 in the Supporting Information), consistent with the findings of others (37–39). Additionally, As in arsenopyrite is in the lowest formal oxidation state of all our standards and thus occurs at the lowest energy (11866.6 eV). Arsenic sulfide species (orpiment and realgar) occurred at higher energies (~ 11869 eV). The sodium arsenite standard occurred at ~ 11871 eV; whereas sodium arsenate was located at the highest energy positions ~ 11874 eV (see Figure 2 in the Supporting Information).

Quantitative analysis was achieved using a linear combination of the standard As phase spectra described above and comparing them to the unknown. A Levenberg–Marquardt least-squares algorithm in the WinXAS code was used to minimize the error between the unknown and “reconstructed” spectrum (41) as described elsewhere (21); multiple starting values were used to confirm that a global minimum in errors was reached. Energy shifts were constrained during fitting to <1.0 eV while minimizing the fit residual.

Selective Chemical Extractions. Selective sequential extractions are common procedures that provide useful information on trace element partitioning within soils and sediments (see reviews in refs 42–44). It is important to note that although sequential extractions attempt to isolate and dissolve one particular soil fraction, the efficiency of chemical extractions depends on the affinity and specificity of the extracting chemical for the target phase. Therefore, soil extractions are at best “operationally defined” and are referred to by their method of extraction and not the target phase (45, 46). Nevertheless, in light of these shortcomings, selective extractions provide valuable information regarding general partitioning patterns and estimates of reactive phases within soils.

Oxygenation of reduced soil upon collection leads to redistribution and repartitioning of contaminants (11, 47). To circumvent this artifact, analyses of reduced phases were performed in a N₂-purged glovebox. Sequential extractions were initiated using homogenized 4 g wet sediment (~ 2 g dry weight equivalent) subsamples from the top 0–2 cm of cores taken from the three sampling sites. Following each extraction, the soil residue was washed with double-deionized water. Supernatants were filtered through a $0.2\text{-}\mu\text{m}$ membrane filter and acidified with concentrated HCl prior to ICP analysis. Extractions were performed in triplicate along with appropriate controls and blanks. Operationally defined Fe and As sums were normalized to provide comparable measures between sampling periods. Relative fractions were determined by summing all extractants to create an operationally defined total. Comparison of a total digestion via HNO₃/HCl/HF with our operationally defined sums demonstrated excellent Fe and As recovery (RSD $<11\%$ for both

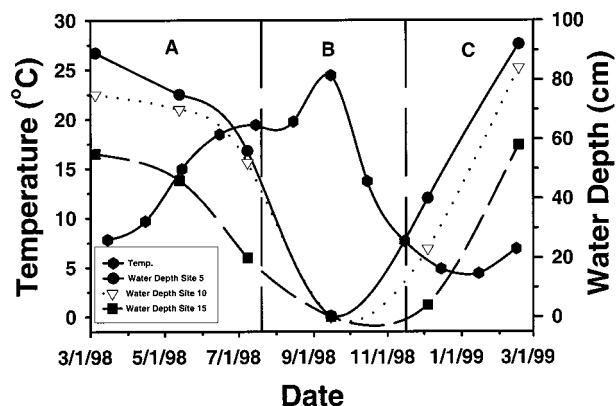


FIGURE 1. Seasonal sediment–water interface temperatures from the middle of the wetland (site 10) and water depths from all three sites.

elements). The extraction procedure utilized in this study aspires to optimize the selectivity of each extraction while preserving sample integrity. Most importantly, however, we seek to define the reactivity of Fe and As within different extractable phases using the defined extraction sequence.

The first step in the extraction series involves the removal of water-soluble and exchangeable Fe and As (inorganic and organic) by the addition of 1 M magnesium chloride (MgCl_2) at pH 7 followed by shaking for 1 h (48). Second, Fe and As associated with the operationally defined carbonate phase were determined using a 1 M sodium acetate/acetic acid (SA/AA) for 5 h extraction (48). Following the sodium acetate/acetic acid extraction, an extraction to remove acid volatile sulfides (AVS) and noncrystalline (hydr)oxides was conducted using 1 M HCl followed by shaking for 12 h (49). The sediment remaining after the HCl extraction was then treated with sodium hypochlorite (NaOCl) at $95 \pm 5^\circ\text{C}$ three times to enhance removal of Fe and As associated with organic matter (50, 51). Next, 1 M hydroxylamine–hydrochloride/acetic acid (HH/AA) was added and allowed to react for 6 h at $95 \pm 5^\circ\text{C}$ to dissolve crystalline (hydr)oxides (48). Removal of the residual silicate fraction was undertaken by reaction with 10 M hydrofluoric acid (HF) for 16 h (49, 52). Finally, the non-AVS (pyritic) extractable fraction was removed by reacting the remaining solids with nitric acid (HNO_3) for 2 h (49, 52).

Results and Discussion

Physical Site Conditions. The average temperature at the sediment–water interface in the wetland increased from 7 to 20°C between early spring (3/1/98) and summer (7/15/98) (interval A, Figure 1). Increased temperatures coupled with elevated microbial activity increase the likelihood for reductive dissolution of iron (hydr)oxides; this will subsequently release sorbed As species to the aqueous phase despite decreased water levels. Water levels were elevated at all sites in the early spring months as a result of rainfall and snowmelt; they then decreased as the wetland warmed. In September (9/15/98), the wetland dried, and the highest sediment temperatures were recorded (25°C) (interval B, Figure 1). During this sampling time, oxidative transformations of the sediment facilitates iron (hydr)oxide precipitation and subsequent oxidation of As may transpire. During fall months, the wetland was replenished with water from rainfall and temperatures decreased. Finally, in winter temperatures decreased to $\sim 6^\circ\text{C}$ (interval C, Figure 1) as the wetland becomes chemically and biologically dormant.

Aqueous Phase. The pH of the water column of the wetland was slightly acidic and averaged between 5.7 and 6.7. Iron and As are detected at appreciable levels in the spring (site 15) and early summer months (sites 5 and 10) (Figure 2A–C). Drinking water standards (DWS) for As are

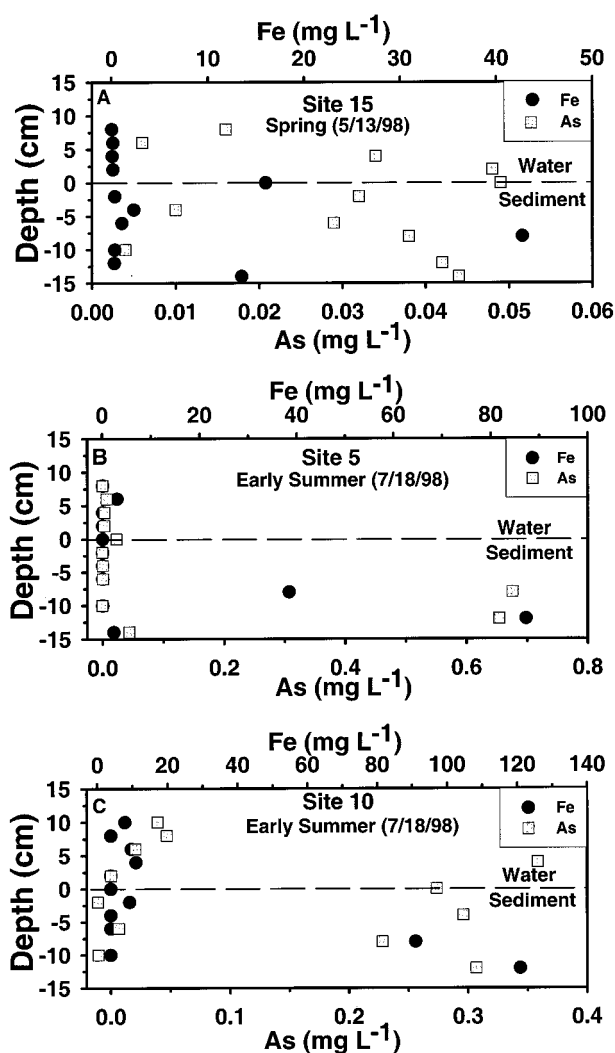


FIGURE 2. Seasonal aqueous-phase Fe and As concentrations from site 15 near cattail vegetation in early spring (5/13/98) (A); at site 5 in the deepest part of the wetland in early summer (7/18/98) (B); and site 10 in the middle of the wetland in early summer (7/18/98) (C).

0.05 mg L^{-1} (53); thus, As is below DWS in the spring (Figure 2A). Iron and As are positively correlated ($r = 0.36$) in the aqueous phase during this sampling interval. However, in summer, Fe and As are significantly ($P < 0.05$) correlated in the deep parts of the wetland ($r = 0.91$) at site 5 and positively correlated ($r = 0.46$) at site 10 (Figure 2B,C). Thus, in the summer, Fe and As have similar trends in solution and As values are higher than DWS (an order of magnitude greater at site 5) at selected depths below the sediment–water interface, possibly in anaerobic microsites where reductive dissolution of iron (hydr)oxides is leading to the release of sorbed As.

Speciation of As in (Bulk) Solids. A decrease in redox potential may imply a reduction of arsenate to arsenite (7, 10, 54). Fitting the XANES spectra of the wetland soils with a linear combination of standard compounds illustrates high variability among As species from the interior portions of the wetland at any given sampling time (Figure 3). Reduced As species (sorbed arsenite and arsenic sulfide phases) existed in the sediment collected from the deeper anoxic parts (site 5) of the wetland in the spring and summer (Figure 3). Moreover, in the spring, there was 22% sorbed arsenite and 78% arsenic sulfide species residing in the solid phase. Frequently, sulfides act as a contaminant sink, and indeed,

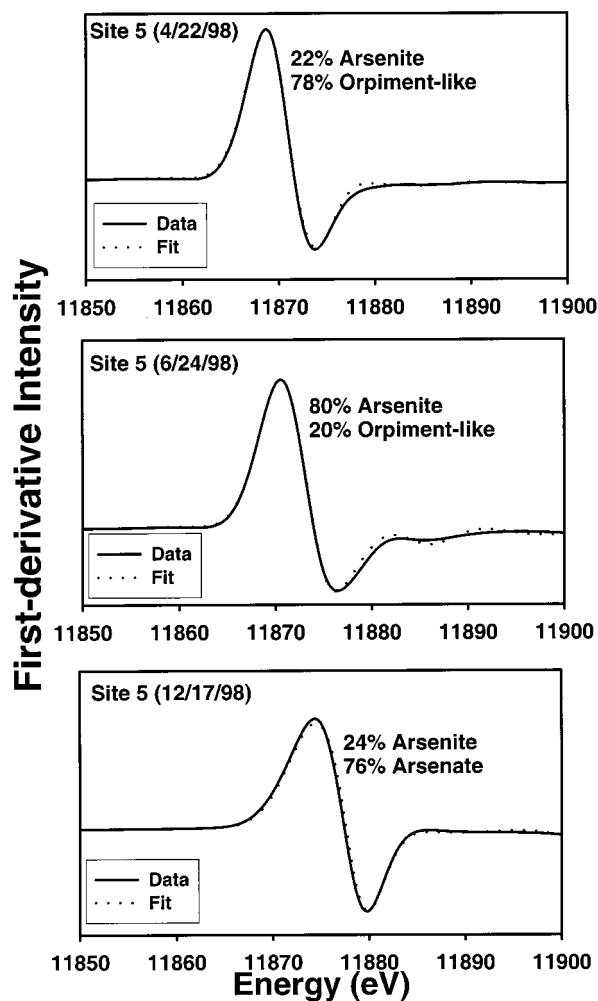


FIGURE 3. Unknown samples and optimal fits based on linear combinations of the standards to the soil solids collected at site 5.

As partitions with sulfidic material in reduced soils (19, 37). Arsenic sulfides may occur as a result of microbial reduction of sulfate and arsenate with concomitant precipitation or from reductive precipitation with excess sulfide, as noted by Rittle et al. (55). Water levels decreased in summer, allowing more oxygen to diffuse into the sediment causing oxidation of arsenic sulfides, leading to the formation of arsenite in the soil solids (Figure 3). Finally, in the winter, after oxidative transformation and inundation with fall rainfall, 85% of solid-phase As existed as arsenate.

Reactive Fe and As Phases. To probe reactive species of arsenic, we used SSE, which provides complimentary information to XANES spectroscopy by assessing the reactivity and distribution of Fe and As in the solid phase. It is important to note that differences in SSE percentages and spectroscopic data may be explained by the limitations of the extractions that include (i) incomplete removal of the target phase, (ii) mineral coatings that essentially shield the host particulate (of which only the host is detected using XANES spectroscopy) from attack by a given reagent, (iii) readsorption and redistribution that may have occurred during the extraction sequence (47, 56, 57).

The seasonal SSE data for all three sites exhibit variable Fe and As trends (Figure 4A–G). A comparison of Fe concentrations detected in the solid phase at all three sites shows that the MgCl_2 (47–1940 mg kg^{-1}), NaOCl (20–337 mg kg^{-1}), and HNO_3 (49–537 mg kg^{-1}) extractable fractions contain appreciably less Fe than the SA/AA (352–11 100 mg

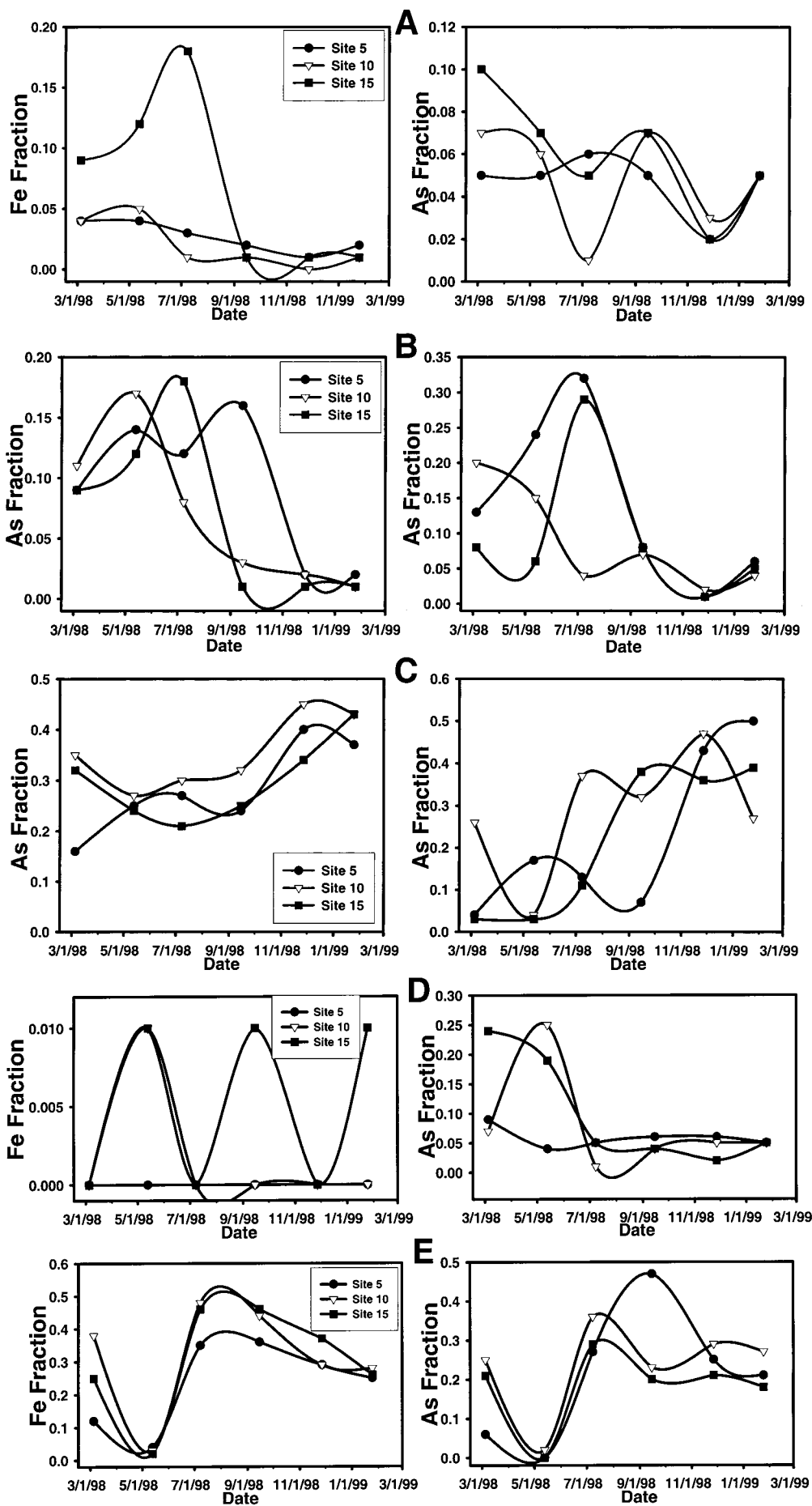
kg^{-1}), HCl (6161–23 836 mg kg^{-1}), HH/AA (840–39 000 mg kg^{-1}), and HF (5240–24 880 mg kg^{-1}) extractable fractions. Arsenic concentrations were lower in the MgCl_2 (2–11 mg kg^{-1}) and HNO_3 (0.5–9 mg kg^{-1}) extractable fractions as compared to the SA/AA (1–40 mg kg^{-1}), NaOCl (1–26 mg kg^{-1}), HCl (0–76 mg kg^{-1}), HH/AA (0–68 mg kg^{-1}), and HF (9–107 mg kg^{-1}) extractable fractions of the solid phase.

The MgCl_2 , NaOCl , and HNO_3 extractions contained minimal amounts of Fe and As (Figure 4A,C,G). However, significant and appreciable trends between these two elements did exist. For example, Fe and As removed using MgCl_2 and HNO_3 were positively correlated (Table 1). Additionally, As fractions reached appreciable levels in the NaOCl extractable pool during the spring as biological activity likely increased (Figure 4D). It is important to note that this extraction can oxidize sulfidic fractions of the sediment, thereby overestimating As associated with this extractable pool (51).

The majority of Fe and As within the wetland was removed with SA/AA, HCl , HH/AA, and HF extractions (Figure 4B,C,E,F). Abundant Fe and As were removed using SA/AA that is designed to remove the carbonate fraction of the soil matrix (Figure 4B). Iron is positively correlated among the sites within this extractable pool (Figure 4B, Table 1). Elevated Fe concentrations in the SA/AA extractable fraction occur during the summer months as the wetland warmed and biological activity increased. There is a documented partitioning of As on calcite surfaces (7, 17, 18, 58), and we noted a positive correlation with its removal using SA/AA (carbonate) extractions. The seasonal trends for As are positively correlated at two sampling sites (Figure 4B, Table 1). Iron and As extracted using SA/AA are positively correlated at all sites (Table 1). The positive correlation between Fe and As in the spring and summer may be explained by an increase in P_{CO_2} , which would facilitate carbonate formation. Thus, freshly precipitating carbonates provide reactive surfaces that can sorb arsenite (detected using XANES spectroscopy) especially during the spring and summer months.

In anoxic portions of wetlands, amorphous sulfides in addition to amorphous (hydr)oxides play an integral role in trace element partitioning (19). Seasonal Fe trends for the sampling sites are significantly ($P < 0.05$) correlated between site 5 and site 10 (Figure 4D, Table 1). In general, Fe decreases in summer within this extractable pool as a consequence of dehydration; it then increases within this pool during the fall as the site rehydrates (Figure 4C). Arsenic removed using HCl is primarily associated with AVS and amorphous (hydr)oxides that may coat the sulfide phases identified using XANES spectroscopy. Investigations of As adsorption on amorphous hydroxides (i.e., ferrihydrite) indicate that there is a high affinity of As for these surfaces (25, 26, 28, 29). Thus, arsenite and arsenate may be sorbed to amorphous materials, presumably an amorphous and short-range order iron (hydr)oxides such as ferrihydrite, during the fall and winter when Fe and As are elevated in this extractable pool.

There is abundant Fe removed using HH/AA that is significantly ($P < 0.05$) correlated at two out of three sampling sites (Figure 4F, Table 1). The abundance of HH/AA (crystalline oxide) extractable Fe suggests that this solid is another important sink for As. The role of iron (hydr)oxides and their influence on As attenuation has been noted by other researchers (6–8, 10). It is not surprising that As is also abundant within this extractable pool and significantly ($P < 0.05$) correlated between site 10 and site 15 (Figure 4F, Table 1). More importantly, Fe and As extracted using HH/AA are significantly ($P < 0.05$) correlated at all three sites (Table 1). We hypothesize that arsenite and arsenate species detected using XANES spectroscopy (Figure 3) may be associated with crystalline iron (hydr)oxides whose fractions increased during the summer months. Thus, the formation and stability of



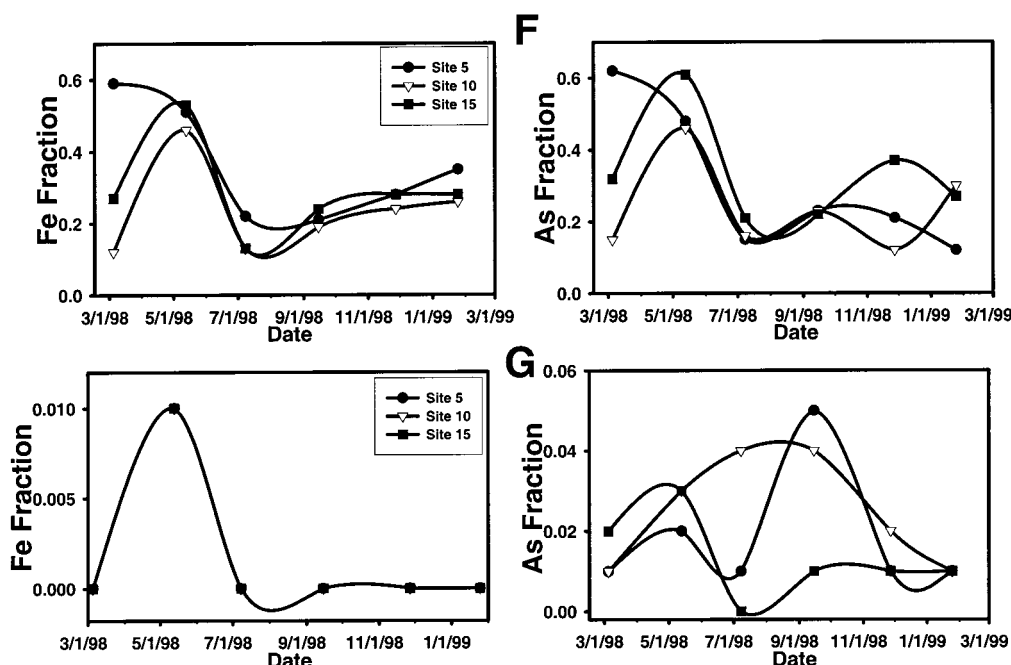


FIGURE 4. Fractions of the total Fe and As removed using a given extractant for all three sites throughout the period of investigation. Magnesium chloride (exchangeable and water soluble) (A), sodium acetate/acetic acid (carbonate) (B), hydrochloric acid (amorphous materials) (C), sodium hypochlorite (organic matter) (D), hydroxylamine–hydrochloride/acetic acid (crystalline oxide) (E), hydrofluoric acid (silicate) (F), and nitric acid (pyrite) (G) extractable fractions of the solid phase.

TABLE 1. Pearson Correlation Coefficients of Seasonal Fe and As Extractable Phases among the Three Sampling Sites

sampling site	MgCl ₂	SA/AA	HCl	NaOCl	HH/AA	HF	HNO ₃
Fe Extractable Phases							
5–10	0.93 ^a	0.52	0.93 ^a	0.94 ^a	0.78	0.29	0.99 ^a
5–15	0.64	0.47	0.70	0.70	0.95 ^a	0.60	0.99 ^a
10–15	0.48	0.71	0.65	0.65	0.92 ^a	0.92 ^a	0.98 ^a
As Extractable Phases							
5–10	0.41	0.26	0.30	−0.46	0.54	0.08	0.54
5–15	0.53	0.81	0.61	0.41	0.57	0.45	0.12
10–15	0.76	−0.12	0.56	0.57	0.98 ^a	0.58	−0.34
Fe and As Extractable Phases							
5	0.58	0.58	0.92 ^a	−0.74	0.93 ^a	0.89 ^a	0.31
10	0.49	0.77	0.59	0.91 ^a	0.87 ^a	0.89 ^a	0.14
15	0.14	0.78	0.53	−0.04	0.89 ^a	0.95 ^a	0.91 ^a

^a $P < 0.05$.

crystalline iron (hydr)oxides directly affect As sequestration within this wetland.

Fluctuations in Fe and As partitioning within HF (silicate) extractable fraction are surprising; we initially expected this pool to remain fairly constant throughout the period of investigation (Figure 4F). It is important to note that appreciable levels (~20% of coarse fraction) of volcanic ash exist within the site. High surface area and reactivity of weathered volcanic ash can sorb Fe and As or lead to secondary silicate precipitates of these elements, thereby increasing their potential for removal at the HF part of the extraction sequence. Iron removed with HF is significantly correlated ($P < 0.05$) between site 10 and site 15 (Table 1). Elevated Fe fractions associated with the HF extractable pool in the spring appear to be inversely related to the HH/AA (crystalline oxide) extractable fraction (Figure 4F,G). We suggest that increased Fe and As removed via HF in spring were associated with preferential sorption to the phyllosilicate clay matrix or volcanic ash, including the possibility of secondary precipitates. Arsenate has a high sorption capacity

for phyllosilicate minerals (e.g., muscovite and biotite), especially near pH 7.0 (17, 20, 22). In addition, As tends to sorb to more recalcitrant solid phases in soil with time (59). Thus, in winter sorbed arsenate detected using XANES spectroscopy is likely adhered to phyllosilicate clay minerals as denoted by an increase in their proportions via removal with HF.

Wetlands are vital but sensitive ecosystems that have the capacity to sequester large quantities of inorganic toxins such as arsenic. Seasonal changes in the chemistry of many wetlands may lead to sporadic pulses of dissolved or potentially bioavailable contaminants such as arsenic. Our present study reveals that Fe and As are co-distributed in the aqueous and solid phase of a mining-impacted wetland and that their reactivity is influenced by changing physico-chemical soil conditions—namely, temperature and water level. The speciation and partitioning of arsenic change seasonally and are correlated with Fe. Arsenic lies in silicate and carbonate extractable pools during late spring to summer and then transitions into an oxide-associated fraction in the late summer to fall that persists into winter. Temporal differences in As species and extractable pools illustrate the potential for transitory release of arsenic and its dynamic nature in wetland environments.

Acknowledgments

We gratefully acknowledge support provided by the Exploratory Research Program of the U.S. EPA (Grant R-825399). We also thank Dr. G. C. Li for assistance in statistical analysis. Special thanks are given to the staff at the Stanford Synchrotron Radiation Laboratory (SSRL). SSRL is operated by the Department of Energy, Office of Basic Energy Sciences; support for the Biotech program is provided by the National Institute of Health.

Supporting Information Available

Two figures showing a location map of the site and the spectra of our As standard compounds used for linear combination fitting (3 pages). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Received for review February 18, 2000. Revised manuscript received June 26, 2000. Accepted July 6, 2000.

ES0010150